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Integrated processing for the separation of biobutanol. Part A: experimental investigation and process modelling

Abstract: *n*-Butanol is an important bulk chemical and a promising potential fuel additive. An alternative way to the chemical production of biobutanol from crude oil is the fermentation of biomass. However, the main drawback of this process is the toxicity of *n*-butanol towards the microorganisms resulting in a limited productivity. Additionally, high purification costs occur due to an energy-intensive distillation step which is used, up to now, as purification technology for the recovery of *n*-butanol. Therefore, alternative separation processes are discussed in this study. Extraction and pervaporation are two unit operations with high potential to overcome this problem. Because of their tuneable properties, the use of ionic liquids as extraction solvents for *n*-butanol recovery is a promising option; however, their economic potential is not obvious because of the relatively high costs. On the basis of those two unit operations, different potential processes to separate biobutanol from water are modelled using experimental data. Cost estimations result in purification costs of €0.230 kg^{-1} to €0.296 kg^{-1} *n*-butanol, which accounts for 20%–27% of the *n*-butanol market price in 2012.

Keywords: biobutanol; extraction; ionic liquid; pervaporation; process analysis.

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1 Introduction

n-Butanol is an important bulk chemical with an estimated global production of around 5.1 million tons $year^{-1}$ (2002) [1]. It is mainly used as solvent for the production of paints and coatings and as intermediate for the production of carboxylic acids [1]. Besides, owing to its high energy contents and antiknock properties, butanol is often discussed as a potential candidate as automotive fuel to replace gasoline [2]. *n*-Butanol is mainly produced by chemical processing of petrochemical raw materials [3]. To establish more sustainable production processes and because of the increasing price of crude oil, production of butanol from renewable resources is gaining increasing interest. One possibility for sustainable production is the fermentation of biomass by microorganisms. The anaerobic fermentation of sugars, starch, or cellulosic raw materials, e.g., by using the microorganism *Clostridium acetobutylicum*, leads to the production of *n*-butanol and formation of ethanol and acetone as the main side products. Hence, this process is also known as acetone-butanol-ethanol (ABE) fermentation [2]. In batch fermentations, product concentrations of around 20 g l^{-1} with a mass ratio of the products of 3:6:1 (acetone/butanol/ethanol) can be achieved. For convenience in the following text, the expression "butanol" is used in terms of biotechnologically produced *n*-butanol.

Besides improving fermentation by the development of new microorganisms, one of the main drivers towards an economic process is the development of an efficient downstream processing. Especially, the separation of the product butanol from water has been identified to be the key to design an economical biobased process [4]. One possibility to separate butanol from the fermentation broth at industrial scale is the use of distillation. However, two major challenges exist. First, the system contains several azeotropes. This means that the separation applying distillation is a complex task and the use of several distillation columns is necessary. Second, the butanol concentration is low and because of the low boiling point of water, the separation by distillation means that the whole water fraction needs to be evaporated. This leads to a high energy demand for the separation. The cost for the separation of butanol by distillation from the fermentation broth causes up to 40% of the total production costs [5]. Hence, alternative energy-efficient unit operations

for the downstream processing are necessary. In the literature, several unit operations have been discussed, which include adsorption, gas stripping, extraction, perstraction, pervaporation and reverse osmosis, which are reviewed in refs. [6–9]. For each of those unit operations, different adsorbents, solvents and membrane materials have been investigated. Each unit operation has its advantages as well as disadvantages and none of them is able to outperform all other unit operations within the whole operating range. Most of the current comparison studies published in the literature have been focused on single separation technologies.

The purification of butanol by extraction is one example of a promising separation process. Already in 1987, Roffler et al. [10] investigated an extractive *in situ* product removal that resulted in increased butanol productivity. Different studies indicate that extraction can lower the energy demand for the separation [9], and thus the production costs, compared with separation by distillation [4]. The economic feasibility of *in situ* extraction depends on the extraction solvent, which influences the separation by its properties as well as the costs by its price. Another example of an alternative butanol separation process next to distillation and extraction is the separation by pervaporation for which Vane [11] published a review on the application of pervaporation for alcohol (methanol, ethanol, butanol, 2-propanol) separation, including economic studies. Most of the reviewed studies claim that pervaporation is the most economical solution for alcohol separation from aqueous streams, or at least at the bounds of competitiveness. However, the results of these studies strongly depend on the assumptions made for permeate fluxes, separation factors, membrane and module lifetime, and costs per membrane area [11]. For the pervaporation of butanol from the fermentation broth in particular, an economic study was published by Schoutens and Groot [12]. Other available studies on butanol pervaporation are often focused only on the energy requirements of the downstream process and thus neglect the cost per membrane area, which is crucial for membrane processes [8, 13, 14].

The selection of the most economic single unit operation for the separation of butanol from water is not possible without taking into account the whole process. Neither a single distillation column nor an extraction or pervaporation process alone can deliver butanol with a high purity. Besides, the integration of two or more unit operations for the separation task is potentially promising to achieve an economic process configuration [15]. For a quantitative comparison of different process configurations, modelling plays an essential role.

Therefore, within this article, a set of integrated processes is formed on the basis of the identification of the most promising unit operations, the modelling of those processes and, if necessary, accompanied by experiments for parameter estimation and model validation. The different investigated integrated process configurations are based on the extraction using ionic liquids and pervaporation for separation of butanol at low feed concentrations, integrated with a distillation process to achieve the desired purity. In simulations, these two processes are compared with a benchmark process, which uses two distillation columns. For the comparison, costs are estimated for all three processes. Note that the cost estimations and thus the process economics might be highly sensitive to uncertain fixed model parameters, model assumptions or price indices.

2 Process configurations

In this section, an overview on the state-of-the-art technologies in ABE fermentation and product separation is given, and the model assumptions made for this investigation are explained. Furthermore, a detailed literature review on possible separation units for the separation of butanol was performed. The most promising among these units were considered for extensive process investigations. Each of the generated process configurations as well as the benchmark design will be explained in more detail in Section 2.3.

2.1 Background fermentation

The production of butanol from biomass is based on the fermentative conversion of carbohydrates by microorganisms. For *Clostridia* microorganisms, the main metabolic products are acetone, butanol and ethanol (ABE fermentation). This metabolic pathway is one of the most extensively studied pathways for butanol production [2]. Until 1950, two-thirds of the world's supply of butanol was obtained from ABE fermentations, meaning that ABE fermentation was the second largest biotechnological process after the fermentation process for the production of ethanol. After 1950, ABE fermentation was no longer economically competitive with the petrochemical synthesis route because of increasing substrate costs and falling oil prices [2]. However, with increasing oil prices, this has changed nowadays and ABE fermentation is again of high interest. Besides the aforementioned

Clostridium acetobutylicum, other microorganisms that convert biomass into butanol have been discovered or engineered by using metabolic engineering techniques in order to increase their tolerance towards higher butanol or higher substrate concentrations or to enhance the selectivity towards butanol. Those microorganisms include, besides others, *Clostridium beijerinckii*, *Clostridium saccharoperbutylacetonicum* and *Clostridium saccharobutylicum* [16, 17]. Sugars in the form of molasses, sugar cane and corn starch are common substrates; however, the use of (hydrolysed) lignocellulosic biomass is also possible [2, 6]. The advantages of the latter are that there is no competition with food production as well as the lower price of cellulose compared with the above-mentioned common substrates [16]. The conversion mechanisms from sugars to ABE can be classified into two phases [18]. In the first phase, the exponential growth phase or acidogenesis, the substrate is converted to intermediate products such as pyruvate, lactate, acetate, butyrate, and the gases hydrogen and carbon dioxide. In the second phase, called the stationary phase or solventogenesis, the acids are converted to the final products acetone, butanol and ethanol. The acids produced within the first phase are reduced simultaneously [17].

Fermentation may be operated in batch, semibatch or continuous mode. The application of batch processes is limited owing to low cell concentrations and product inhibition, which lead to reduced productivities [17]. Typical laboratory-scale process parameters of batch processes for ABE production are presented in Table 1.

The productivity of ABE is very low, and also the use of fed-batch processing only doubles the productivity. The butanol concentration within the ABE formed is always around 60%. With the aim to increase the productivity of the process, fermentation in a semicontinuous mode has been investigated in which several fermenters are connected in a cascade [22]. Thus, the substrate supply and purification of the broth can be carried out continuously while the fermentation itself still runs in a batch mode. Typical results of continuous ABE fermentations are presented in Table 2. Comparing the productivity of ABE and butanol of the semicontinuous mode with the batch operation using the organisms, a higher productivity can be achieved; however, the concentrations of the products decrease.

Besides different investigations, several industrial-scale ABE processes have also started operation within the last years. In Brazil, a new plant is built with an annual capacity of 8000 tons of ABE produced from sugar cane. Plants in China started production again in 2010 after they ceased production in 2008 because of an oil price crash [26]. In Russia, first large-scale trials were performed using hydrolysed lignocellulosic waste [27]. In China, six new plants and five retrofitted plants have started operation, while five more are currently planned or under construction [28]; the annual capacity of a plant is reported to exceed 100,000 tons of ABE. In the United States, American Process Inc., and Cobalt Technologies constructed a fermentation process using hemicellulose from cellulosic biomass [29]. In Alpena, Michigan, an ABE plant for the production of around 1440 tons of butanol was built [29]. Table 3 summarises the process parameters of three different fermentations at industrial scale. In the United Kingdom, DuPont and BP currently investigate *n*-butanol and isobutanol production under the joint venture Butamax™ Advanced Biofuels. The commissioning of a plant for the commercial production of isobutanol was planned for 2012 or 2013 [30].

2.2 Separation systems for butanol recovery

Butanol is an aliphatic saturated alcohol and exists in four isomeric structures: the primary alcohols butanol and 2-methyl-1-propanol (isobutanol), the secondary alcohol 2-butanol, and the tertiary alcohol 2-methyl-2-propanol.

Table 1 Batch fermentations at laboratory scale.

Organism		*Clostridium acetobutylicum*		*Clostridium beijerinckii*
Substrate	**(-)**	**Glucose**	**Glucose/maltodextrin**	**Glucose (conc.)**
Operation	(-)	Batch	Batch	Batch
ABE productivity	($gl^{-1}\ h^{-1}$)	0.34	0.58	0.61
Butanol productivity	($gl^{-1}\ h^{-1}$)	0.20	0.38	0.40
ABE concentration	(gl^{-1})	24.2	29.0	75.9
Butanol concentration	(gl^{-1})	14.5	19.0	50.1
Time	(h)	–	–	201
Reference		[19]	[20]	[21]

Table 2 Continuous fermentations at laboratory scale.

Organism		*Clostridium acetobutylicum*		*Clostridium beijerinckii*		*Clostridium saccharoperbutylacetonicum*	
Substrate	**(-)**	**Glucose**	**Starch**	**Glucose/maltodextrin**	**Glucose**		
Operation	**(-)**	**Cont., 2 stages**	**Cont., 2 stages**	**Cont.**	**Cont., 2 stages**	**Cont.**	**Cont., cell recycle**
ABE productivity	(gl^{-1} h^{-1})	0.83	3.30	1.74	1.24	1.85	11.00
Butanol productivity	(gl^{-1} h^{-1})	0.50	1.98	1.15	0.74	1.11	6.60
ABE concentration	(gl^{-1})	18.3	15.0		9.3	9.3	12.9
Butanol concentration	(gl^{-1})	12.6	7.0		5.6	5.6	7.7
Time	(h)	60	–	100	–	–	48
Reference		[23]	[22]	[20]	[24]	[25]	[25]

Table 3 Overview of fermentations at industrial scale.

Organism		*Clostridium acetobutylicum*		
Substrate	(-)	Mixture of corn, wheat and rye	–	Hydrolysed molasses
Operation	(-)	Cont.	Cont.	Cont.
ABE productivity	(gl^{-1} h^{-1})	0.69	20–50% higher than batch processing	n.a.
Butanol productivity	(gl^{-1} h^{-1})	0.41	n.a.	n.a.
ABE concentration	(gl^{-1})	20.9	n.a.	n.a.
Butanol concentration	(gl^{-1})	12.5	n.a.	n.a.
Time	(h)	192	170–480	n.a.
No. of fermenters	(-)	11	6–8	26 in 4 batteries
Volume of one fermenter	(m^3)	3.5	200–500	225–275
Total volume	(m^3)	38.5	n.a.	2000 per battery
Reference		[22]	[28]	[27]

All isomers are soluble in common organic solvents and, apart from 2-methyl-2-propanol, all components form a miscibility gap with water [31]. The important properties of butanol and water are summarised in Table 4. Differences in pure component properties enable the investigation of different unit operations, which are explained in more detail in the following subsections.

It is important to note that water and butanol form an azeotrope as well as a miscibility gap, the so-called heteroazeotrope (see Figure 1). At atmospheric pressure, the azeotrope contains 75.3 mol.% water.

Table 4 Properties of butanol and water [31–33].

Property		Butanol	Water
Molecular weight	M ($g\ mol^{-1}$)	74.122	18.015
Melting point	T_m (°C)	-89.32	0.00
Boiling point	T_b (°C)	117.7	99.97
Density	ρ ($kg\ m^{-3}$)	809.8	998.5
Viscosity	η (10^{-3} Pa s)	3.0	1.005
Vapour pressure	p_{0i} (Pa)	605.2	2337.7
Surface tension at T=20°C	γ (10^{-3} $N\ m^{-1}$)	7.7	72.8
Solubility in water at T=20°C	w_{BuOH} (-)	0.078	–
Solubility in butanol at T=20°C	w_{H2O} (-)	–	0.2

2.2.1 Distillation

The separation of butanol from water by exploiting the differences in relative volatility using distillation is possible until the azeotropic concentration is reached. Because of the low boiling azeotrope (92.4°C), water and purified butanol can only be obtained at the bottom of the

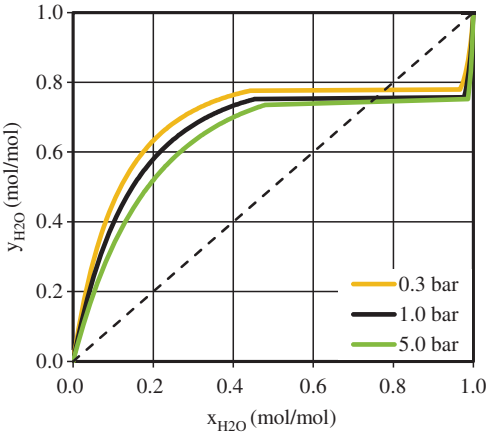

Figure 1 Vapour-liquid equilibrium of butanol and water at different pressures, calculated using Aspen Properties®.

columns when separating binary mixtures. The azeotrope (see Figure 1), which is only slightly pressure sensitive, may be broken by a two-stage distillation configuration (see Section 2.3.1). Additionally, azeotropic distillation may be used, adding a solvent such as decanol, which forms azeotropes with the contained components (with the exception of acetone) [34]. Kraemer et al. [4] have shown that >80% of the total energy demand of a distillation sequence is necessary for solvent separation from the aqueous stream. To get a first idea of the production costs for the distillation-based process, a binary mixture of water and butanol was considered for the process evaluation and cost estimation. When by-products such as acetone, ethanol or organic acids are considered, the distillation sequence becomes more complex [28]. However, the energy required for further purification of acetone, butanol and ethanol is much smaller than for the separation from the aqueous stream [4].

2.2.2 Adsorption

In general, the key challenge within the application of adsorption for the separation or purification of a component is the identification of a suitable adsorbent, which should have a high affinity for the solvent and a low affinity for the substrate and reaction intermediates. For the separation of butanol from the ABE fermentation broth, several adsorbents such as activated carbon [35], charcoal and XAD-type resins [36], as well as zeolites and metal-organic-framework adsorbents [37] have been tested; however, thus far, no satisfactory results with respect to selectivity towards butanol and capacity were achieved [35, 36]. To enable adsorbent regeneration, temperature-swing or pressure-swing processes are needed [9].

2.2.3 Gas stripping

Gas stripping is a relatively simple method to recover products from a fermentation broth. A gas stream is passed through the fermenter directly using gases such as H_2 and CO_2 that are formed during the fermentation process [38]. Alternatively, a gas stream (fermentation gases or nitrogen) can be passed through the fermentation broth in a stripping column outside the fermentation. The purified fermentation broth can be fed back into the fermenter. Preferably, the more volatile components are transferred to the gas phase. In a subsequent apparatus, the gas stream is condensed to recover the solvents (and water), whereas the stripping gases (H_2, CO_2, or N_2) are non-condensable. A disadvantage of gas separation is the low selectivity of the separation towards butanol as intermediates and especially water are also stripped from the fermentation broth. Furthermore, if gas stripping is integrated directly to the fermenter, the productivity might be decreased owing to an enhanced foam formation, which would require the addition of an antifoaming agent. Nevertheless, it must be mentioned that gas stripping can be realised easily and that the continuous butanol removal increases the productivity [39]. Gas stripping was successfully operated in combination with batch [40], fed-batch [41], continuous [42] and fluidised bed reactors [43].

2.2.4 Liquid-liquid extraction

Liquid-liquid extraction is a separation process in which two (almost) immiscible phases are contacted and the solute – in this case butanol – from a liquid feed mixture is transferred to a second phase (solvent phase). To obtain a pure product, the solute has to be removed from the solvent phase (extract) in a subsequent separation step. One of the challenges is to identify a solvent with the following main properties/characteristics: not miscible with the feed phase (here, water), high distribution coefficient for butanol, high selectivity (no removal of substrates and intermediates), a sufficient density difference between the immiscible phases, stability, easy separation of the products in subsequent separation steps and a low price [44]. The butanol distribution coefficient is defined as the ratio of the butanol weight fraction in the extract phase and the butanol weight fraction in the aqueous raffinate [Eq. (1)].

$$D_{\mathrm{BuOH}} = \frac{w^{\mathrm{IL}}_{\mathrm{BuOH}}}{w^{\mathrm{aq}}_{\mathrm{BuOH}}} \tag{1}$$

The selectivity of butanol towards water is calculated by the ratio of the butanol distribution coefficient and the water distribution coefficient [Eq. (2)].

$$S = \frac{D_{\mathrm{BuOH}}}{D_{\mathrm{H2O}}} \tag{2}$$

For the extraction of a solute from aqueous phases, a number of organic solvents are known, showing immiscibility with water. Hence, a lot of organics were investigated for the separation of butanol with respect to selectivity, distribution coefficients and toxicity towards *Clostridia* [9, 45], which can be subdivided into three main groups: oils, alcohols and alkanes. Oils are non-toxic to the organisms, show moderate to high selectivities, but poor distribution coefficients <1 except for castor oil (D=2.6). By choosing an alcohol, the distribution coefficient can

be increased drastically (up to D=12) but the selectivity towards water decreases at the same time. However, not only butanol but also most of the alcohols are toxic to *Clostridia*. One exception is the fatty alcohol oleyl alcohol, which gives a distribution coefficient of D=3.0 and a selectivity of S=195. Alkanes are non-toxic, too. They are nearly insoluble in water, which results in very high selectivities up to S=4300. However, the capacity for butanol is low, which gives poor distribution coefficients of 0.3–0.5 [9, 45].

Besides classic organic solvents, ionic liquids were studied for the purification of butanol. Ionic liquids are salts that are composed solely of ions. Their melting point is below 100°C and vapour pressure is negligibly low below their decomposition temperature [46]. Ionic liquids are composed of anions and cations. By variation of the ions, different liquids are made and thus properties are influenced and the ionic liquids can be adapted to a specific separation task [47]. For the purification of butanol from aqueous solutions, different ionic liquids are reported [48–50]. Fadeev and Meagher [51] studied the ionic liquids $Im_{4,1}$ PF_6 and $Im_{8,1}$ PF_6. The investigations resulted in a distribution coefficient of D=1.72 and a selectivity of S=34 (experimental conditions: temperature of 50°C, weight fraction butanol in aqueous feed 0.05 kg kg^{-1}) for $Im_{4,1}$ PF_6. Ha et al. [52] screened $Im_{6,1}$ CF_3SO_3, $Im_{8,1}$ CF_3SO_3, $Im_{6,1}$ BF_4, $Im_{8,1}$ BF_4 and $Im_{6,1}$ fap. The best results with regards to the distribution coefficient were achieved with $Im_{8,1}$ BF_4: D=2.48 with a selectivity of S=13 (experimental conditions: temperature of 50°C, weight fraction butanol in aqueous feed 0.06 kg kg^{-1}). Santangelo et al. [53] published a distribution coefficient of D=4.29 and selectivity of S=135 for $Im_{10,1}$ tcb (experimental conditions: temperature of 35°C, weight fraction butanol in aqueous feed 0.02 kg kg^{-1}). In 2012, Garcia-Chavez et al. [54] published a screening study in which TOA MNaph had the highest distribution coefficient with D=21 at a selectivity of S=274 (experimental conditions: temperature of 35°C, weight fraction butanol in aqueous feed 0.02 kg kg^{-1}). However, not only distribution coefficients and selectivities are important. The duration for phase splitting is important when a multistage extraction should be applied. Therefore, viscosities, density differences and interfacial tension between water and ionic liquid also become important [44].

2.2.5 Pervaporation

Pervaporation is a process that can selectively separate volatile substances from a solution with the aid of a membrane. The components dissolve into the membrane material, diffuse through the membrane and vaporise on the other side of the membrane (permeate side). The separation of different components in a liquid solution is based on the ability to dissolve into the membrane as well as to diffuse through the membrane. The driving force for the transport is generated by lowering the partial pressure for the components to be separated. This can be realised by diluting the permeate-side concentrations by using a sweep gas or by application of vacuum to the permeate side [55]. Various membrane materials are reported to be applied for separating butanol from water, including poly(dimethylsiloxane) (PDMS), poly(ether block amide) (PEBA) and poly(-1-trimethylsilyl-1-propyne) (PTMSP) [14, 56, 57]. To further improve the competitiveness of the pervaporation and overcome the trade-off between flux and selectivity, new composite materials of polymers and zeolites, carbon nanotubes or ionic liquids are developed [58–60]. Good overviews about organophilic pervaporation are given, e.g., by Oudshoorn et al. [9], Vane [11] or Liu et al. [61]. While dewatering of solvents by means of pervaporation is a well-studied process, the separation of alcohols from aqueous streams is still carried out only in laboratory scale, owing to lower fluxes and selectivities and the risk of fouling when using fermentation broth as feed. Izák et al. [62] integrated an ABE fermentation with a pervaporation process using a supported ionic liquid membrane. The continuous butanol removal enabled continuous fermentation for >16 days and was only terminated because pervaporation was stopped. van Hecke et al. [63] operated a two-stage continuous fermentation over a period of 48 days by removing butanol through pervaporation. They successfully proved that pervaporation can be used to avoid the toxicity limit and increase the fermentation productivity without observing any fouling of the PDMS membrane. According to this, Qureshi and Blaschek [64] observed that silicone membranes were not fouled by two different fermentation media during pervaporation experiments. In contrast to this, Liu et al. [61] observed fouling when using a self-made PDMS/ceramic composite membrane connected to a fermentation. However, this fouling could easily be removed by simple rinsing with water. Claes et al. [14] report about self-made PTMSP membranes, which show ~2.7-fold increased fluxes and selectivities for butanol over water compared with a commercially available PDMS membrane. Unfortunately, these membranes also suffered from fouling more extensively than PDMS membranes [65].

2.2.6 Preselection of promising candidates

For the removal of low-concentrated butanol from the fermentation broth, several separation methods have been investigated. The conventional purification by distillation

involves high energy costs because of low butanol concentrations as well as the higher boiling point of butanol compared with water. Besides the high operating costs, the capital costs are also large as the evaporation of the large amount of water and the high enthalpy of vaporisation of water result in large required evaporator capacities [9]. For one ton of purified products (ABE), a total of 13–25 tons of steam is needed [28]. Besides the separation technologies discussed in Sections 2.2.1–2.2.5, it should be mentioned that additional other methods such as liquid-liquid phase separation by adding salts [66], cooling crystallisation [9], reverse osmosis [36], perstraction [36] or supercritical extraction with carbon dioxide [67] have also been discussed. In previous studies, the separation methods with the highest potential have been identified to be pervaporation, liquid-liquid extraction and adsorption [8, 68]. In Table 5, a qualitative comparison between the different water-butanol separation technologies is summarised, taking capacity, selectivity, fouling (stability of the process) and technical maturity as key categories to preselect the separation processes. Distillation and extraction are common processes that have been realised in the large scale many times. Pervaporation for the dehydration of alcohol/water mixtures, especially ethanol/water, is also used commercially and, hence, has also received a high maturity [73]. According to Qureshi et al. [36], adsorption shows the lowest energy demand for butanol recovery but might suffer from fouling. In comparison, stripping shows the highest energy consumption of all separation processes. Only distillation, extraction and pervaporation score well in all categories and are therefore considered for further detailed investigations and process analyses within this article.

2.3 Processes

On the basis of the selected unit operation, extraction, pervaporation and distillation, three different process configurations were generated that allow the recovery of pure butanol from a water-rich stream. As the recovery of solvents from the fermentation broth is the most energy-consuming step in the whole separation process, only the separation of butanol from water is investigated while by-products and their further purification are not considered in this article [4]. Certain assumptions are taken into account regarding the biological basis of butanol. Further assumptions include the use of stable membrane materials as well as solvents and specifications made for the process design, which are illustrated in more detail in Section 3.

2.3.1 Benchmark process

Butanol and water have, as mentioned in Section 2.2, a heterogeneous azeotrope. To separate the butanol/water mixture into pure components, two columns are required [74] as shown in Figure 2. In the first column, C1, the water-rich feed mixture is purified, achieving the minimum boiling azeotrope of butanol and water at the top of the column and pure water at the bottom. The vapour is fully condensed. In a following decanter, the liquid stream with azeotropic composition splits into two liquid phases. The aqueous phase is recycled back to the first column and the butanol-rich phase is fed to a second distillation column C2. Because the butanol concentration of the organic phase is higher than the azeotropic concentration, pure butanol is obtained as the bottom product while the azeotrope of water-butanol is obtained as the distillate product in the second column. The azeotropic vapour is condensed and recycled back to the decanter. Two heat exchangers at the bottom of the columns are used for cooling the bottom streams from boiling temperature to a temperature of 35°C.

2.3.2 Integrated extraction-distillation process

One alternative process next to the benchmark process is an integrated extraction-distillation process (see Figure 3). The aqueous feed is pumped into a multistage

Table 5 Qualitative benchmarking of separation technologies for butanol separation from fermentation broth [8, 9, 68].

Unit	Capacity	Selectivity	Fouling	Maturity	References
Distillation	High	High (azeotrope)	n.a.	High	[28]
Extraction	High	High	Low	High	[10, 45]
Pervaporation	Medium	High	Low/medium	High	[60, 69, 70]
Supercritical extraction	Medium	High	n.a.	Low	[71]
Stripping	Medium	Low	Low	High	[24, 72]
Adsorption	Medium	Low	High	Medium/high	[35, 36]
Perstraction	Low	Low	Low	Low	[36, 45]

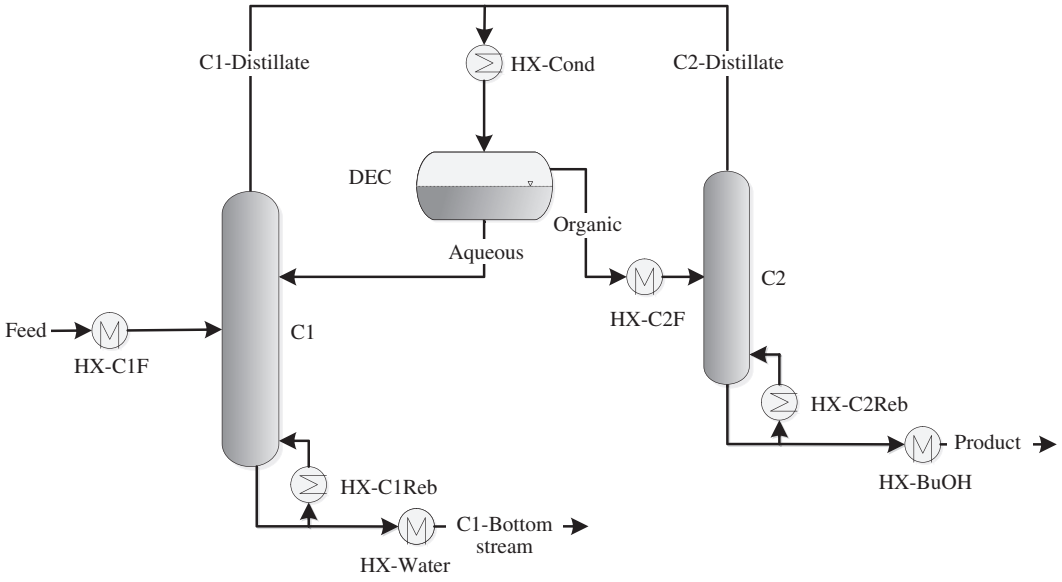

Figure 2 Heteroazeotropic distillation for the separation of a water-rich mixture of water and butanol.

extraction column EXT. Butanol is extracted from the feed into an extraction solvent. For the investigations, the ionic liquid $Im_{10,1}$ tcb is used, which has already been investigated experimentally by Santangelo et al. [53] and Domańska and Królikowski [75]. The extraction is operated in countercurrent mode. The water-rich raffinate leaves the process while the ionic liquid-rich extract is fed to the flash column C1. In this flash, the ionic liquid is regenerated by evaporation of water and butanol dissolved in the ionic liquid. The non-volatile ionic liquid is recirculated to the extraction column where it is mixed with fresh solvent to compensate losses through the raffinate stream. The vapour is condensed in the decanter DEC. As the water-butanol system shows a miscibility gap, the condensate splits into a water-rich and a butanol-rich phase. The water-rich phase is mixed with the aqueous feed entering the extraction unit. The butanol-rich phase is purified in the distillation column C2. While the distillate is composed of a water-butanol mixture, the bottom stream gives almost pure butanol. The distillate is mixed with the distillate leaving the flash column.

2.3.3 Integrated pervaporation-distillation process

Another alternative process is an integrated pervaporation-distillation process (see Figure 4). The binary feed

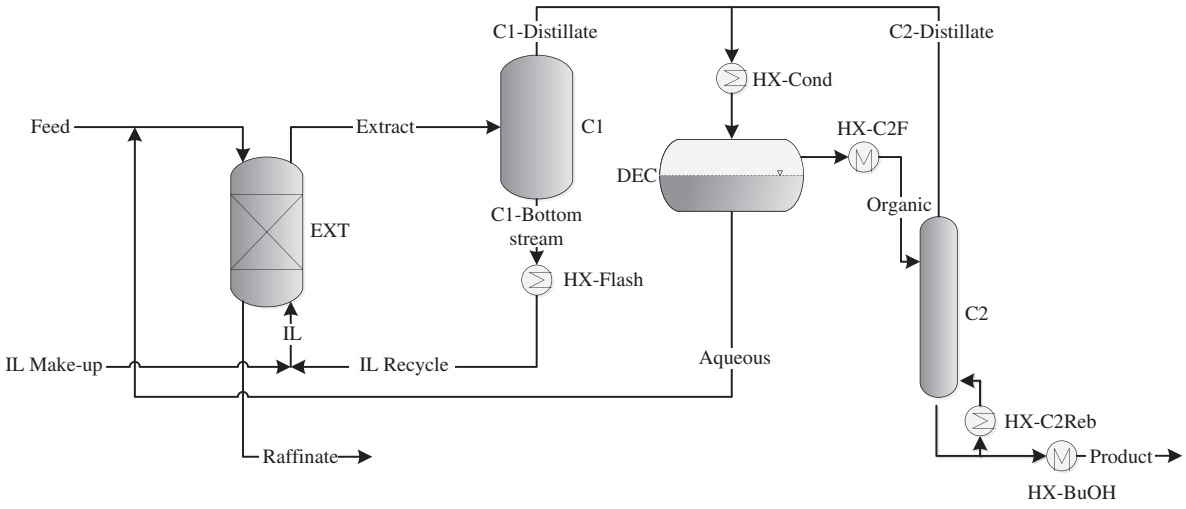

Figure 3 Integrated extraction-distillation process.

mixture of butanol and water is fed to the pervaporation unit PV, in which the butanol and a part of the water permeates through the membrane and evaporates owing to the applied vacuum. Because of the evaporation of the permeate and the associated required enthalpy of evaporation, the feed solution cools down while flowing along the membrane. Before recycling of the retentate depleted in butanol back to the fermenter, it has to be heated up to fermentation temperature again. The permeate is condensed, pumped out of the vacuum section and fed to the decanter DEC. Because membrane processes – similar to the extraction process – are not limited to a vapour-liquid equilibrium, no upper concentration limit exists for the stream entering the decanter. Similar to the benchmark process, the organic phase is further purified by distillation, whereas the aqueous phase is fed back to the inlet of the pervaporation unit. In the distillation column C, the organic phase is split into a vapour fraction with azeotropic composition, which is fed back to the decanter, and into purified butanol, which is obtained as a bottom product.

3 Process modelling and experiments

The following section discusses all models for the different unit operations occurring in the processes under investigation. As a thermodynamic model, the non-random two-liquid (NRTL) model was chosen, being able to describe liquid-liquid as well as vapour-liquid equilibria, and especially the miscibility gap in systems containing water, alcohol and ionic liquid [76]. NRTL parameters were taken from databanks and the literature [75]. Because reliable parameters for the membrane describing concentration, temperature and permeate pressure dependencies have not been found in the literature, they have been determined on the basis of our own experiments. All models were implemented in the simulation environment Aspen Plus® (Aspen Technologies, Inc., Cambridge, MA, USA) except for the pervaporation for which Aspen Custom Modeler® (Aspen Technologies, Inc., Cambridge, MA, USA) was used. In Section 3.5, all cost correlations are listed, which were used to evaluate the total cost of operation (TOC) and the total investment costs (TIC) for the processes, which sum up to the total costs (TC) for purification.

3.1 Distillation

In each process, at least one distillation column is used. All of them are implemented as equilibrium RadFrac models in Aspen Plus®. Considering the biotechnological background of this investigation, the fermentation broth could theoretically foul the column internals. Therefore, the binary system is separated in tray columns, which are less sensitive to fouling effects compared with packed columns. For the vapour-liquid equilibrium, the NRTL VLE-HOC (Hayden-O'Connel) parameter set within Aspen Plus® (V7.2) is chosen, which is able to describe the water-butanol system. The NRTL parameters are given in Table A2 in the appendix. The distillation columns are assumed to run without any heat losses.

3.2 Extraction

The equilibrium extraction model of Aspen Plus® is used to simulate the liquid-liquid equilibrium between an aqueous phase and an ionic-liquid phase within the

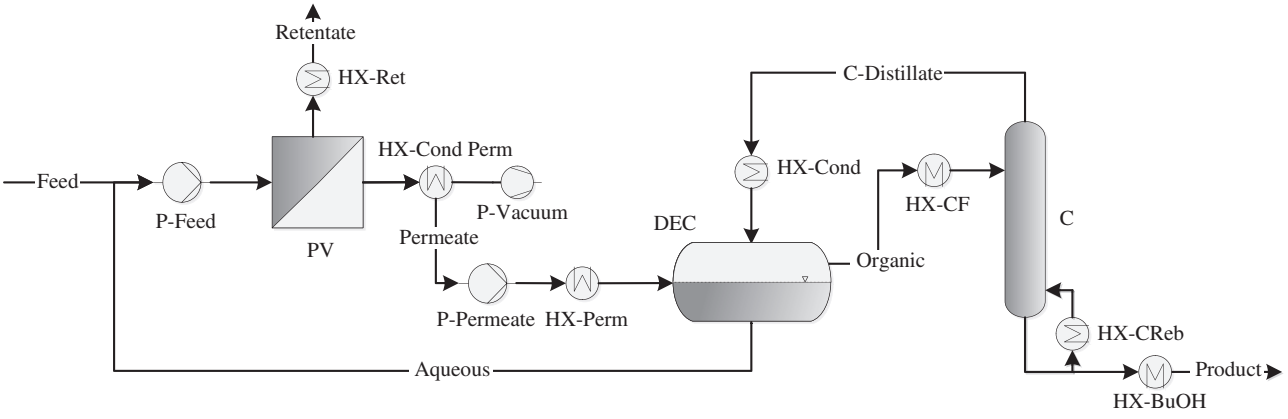

Figure 4 Integrated pervaporation-distillation process.

integrated process. The ionic liquid $Im_{10,1}$ tcb is chosen as the extraction solvent (see Section 2.3.2). Owing to the lack of property parameters for the ionic liquid in the Aspen databanks, they have to be implemented manually.

The binary interaction parameters of the present ternary system $Im_{10,1}$ tcb-water-butanol at 35°C are taken from Domańska et al. [75]. They are given in Table A3 in the appendix. The molecular weight of the ionic liquid is 338.26 g mol^{-1}. The liquid heat capacity of the ionic liquid is calculated with the correlation of Farahani et al. [77].

3.3 Pervaporation

As described in Section 2.2.5, numerous membrane materials are available for pervaporation of butanol. Because PDMS membranes are reported to be less susceptible to fouling, a commercial PDMS membrane (Sulzer Pervap™ 4060, Sulzer Chemtech, Allschwil, Switzerland) was chosen. This membrane was investigated for separation of butanol from aqueous media by Marszalek et al. [78] and Claes et al. [14] at temperatures >50°C. To create a comprehensive and consistent data basis for process modelling, our own pervaporation experiments were carried out varying the pervaporation temperature (37°C≤T≤75°C), permeate pressure (10 mbar≤p_{Perm}≤50 mbar) and the butanol feed concentration (0.00 g g^{-1}≤$w_{Feed,BuOH}$≤0.03 g g^{-1}). Details about the experimental procedure, the setup and analytics are described elsewhere [60].

3.3.1 Experimental results

Within this section, the influence of the feed concentration of butanol and water, the temperature and the pressure on the partial fluxes of butanol and water is discussed. The results are presented in Figure 5. The partial fluxes of butanol increase with the feed concentrations linearly (Figure 5A). They also increase with the temperature. At a temperature of 37°C and a permeate pressure of 30 mbar, a maximal butanol flux of 300 g m^{-2} h^{-1} and a maximal mass fraction of butanol in the permeate of 0.38 g g^{-1} were observed. A temperature increase to 75°C resulted in a 6-fold increase in butanol fluxes. The highest flux measured for a temperature of 75°C was >1300 g m^{-2} h^{-1} at a permeate pressure of 30 mbar; a lower permeate pressure leads to even higher fluxes. For the partial fluxes of water, one would expect that the flux does not increase

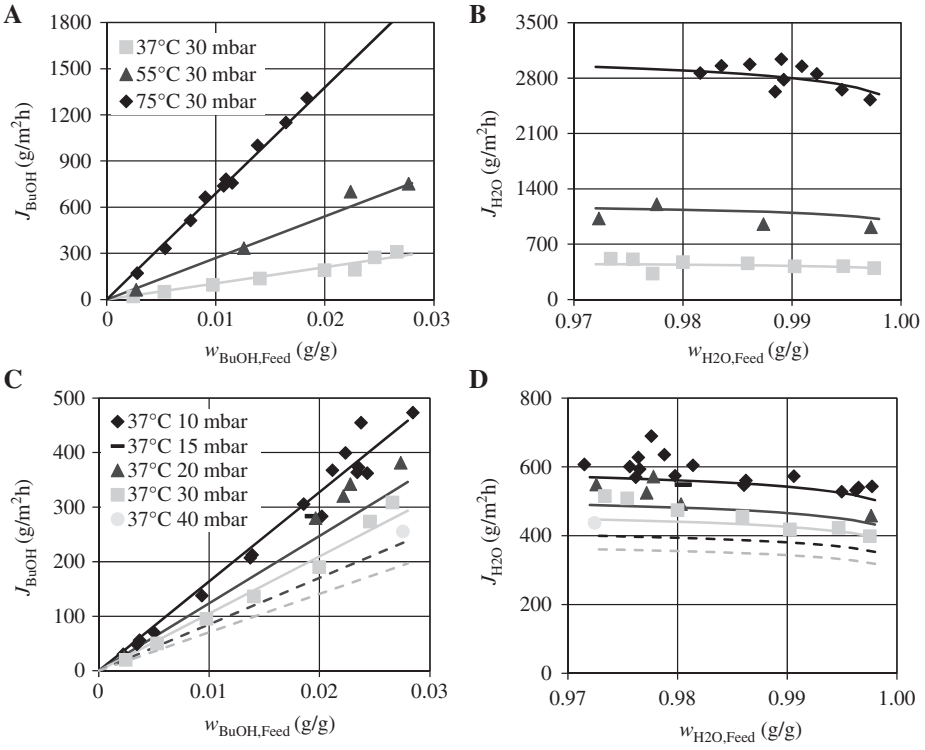

Figure 5 Influence of temperature and feed concentration of butanol (A) and water (B), as well as pressure and feed concentration of butanol (C) and water (D) on the partial fluxes of butanol and water.
Data points represent experimental results and lines were correlated using the correlation described in Section 3.3.2.

with a higher feed concentration of water because the concentration and thus the driving force for permeation of water changes only scarcely. However, in contrast to this, it was observed during experiments that the partial fluxes of water slightly increase with a decreasing water concentration (Figure 5B). As lowered water concentrations are directly linked to higher butanol concentrations in the feed, the explanation for these observations might be an enhanced swelling of the membrane in the presence of higher concentrations of butanol. The swelling of the hydrophobic membrane by butanol renders the membrane more polar and thus improves the permeability of water slightly. However, the effect of the feed butanol concentration onto the partial flux of water is much smaller than for the partial flux of butanol. Therefore, the resulting butanol permeate concentrations are directly dependent on the feed concentrations of butanol. With increased temperatures, the partial fluxes of butanol and water increase by a similar order of magnitude; thus, the permeate concentrations are nearly independent on the pervaporation temperature. The maximum mass fraction of butanol in the permeate was determined to be 0.44 g g^{-1} at a feed mass fraction of 0.028 g g^{-1}. As expected, the highest permeate fluxes of butanol were determined for the lowest vacuum pressure (Figure 5C). By lowering the permeate pressure from 30 to 10 mbar, the butanol flux can be raised by about 50%. The influence of the permeate pressure on the partial flux of water is somewhat smaller than for butanol (Figure 5D).

3.3.2 Partial flux correlation

In pervaporation permeation fluxes, J_i can be described as a product of permeance Q_i and driving force ΔDF_i [Eq. (3)]:

$$J_i = Q_i \cdot \Delta DF_i \tag{3}$$

Differences in the chemical potentials, activities or partial pressures between feed and the permeate side are employed as the driving force, which consider the influence of feed concentrations, temperatures, pressures and non-idealities on the permeation behaviour [11, 79, 80]. However, also the permeance itself depends on concentrations, temperatures and the permeate pressure, which influence the absorption and desorption behaviour of components into or out of the membrane material and therefore the permeability of the membrane, resulting in more or less complex equations if physical backgrounds are considered [80]. Because the complex interactions between membrane material and permeating components cannot be examined only by pervaporation experiments, in this work an empirical correlation was developed to describe the experimentally determined partial fluxes (Section 3.3.1). The partial fluxes of butanol J_{BuOH} are all linearly dependent on the feed mass fraction of butanol $w_{BuOH,F}$ (Figure 5A,C). This means that the magnitude of permeation Q_i is characterised using a constant parameter, Q_i^*. The influence of the temperature is considered by an Arrhenius term with constants E_A and a reference temperature T_0=273.15 K. The dependency on permeate pressure is considered by an exponential function with the constant $A_{p,i}$. As described in Section 3.3.1, the swelling of the membrane by butanol influenced the permeation of water, which is considered in the correlation by the introduction of a factor $\left(1+w_{j\neq i}^{B_{s,i}}\right)$. Owing to the higher polarity of water compared with butanol and PDMS, it is assumed that the permeation of butanol is not influenced by swelling of the membrane by water ($B_{s,BuOH}$=0). On the basis of all these contributions, the developed correlation for the partial fluxes is given in Eq. (4).

$$J_i = Q_i^* \cdot w_{i,F} \cdot e^{E_A / R(1/T_0 - 1/T)} \cdot \left(p_p \cdot [\text{bar}]^{-1}\right)^{A_{p,i}} \cdot \left(1+w_{j\neq i}^{B_{s,i}}\right) \tag{4}$$

The constants Q_i^*, $A_{p,i}$ and E_A were determined by fitting to the experimental results using the sum of least squares as objective function. All parameters are given in Table 6. Because the partial fluxes of butanol and water showed a similar temperature dependency, the constant E_A was set to an equal value for butanol and water. The deviation of the model and the experimental data is for the majority of experimental data points smaller than ±10%.

3.3.3 Pervaporation model

The correlation of the partial flux is integrated into a pervaporation model available in the simulation environment Aspen Custom Modeler® [81]. On the basis of feed streams and compositions, it is possible to determine specific membrane areas for a given separation task or calculate permeate fluxes for a defined membrane area. The discretisation of the membrane area enables the consideration of changes in concentrations and temperatures along a

Table 6 Parameters for the partial flux correlation of butanol and water through a PDMS membrane.

	Unit	Butanol	Water
Q_i^*	g m^{-2} h^{-1}	243.43	14.46
E_A	kJ mol^{-1}	44.496	44.496
$A_{p,i}$		-0.406	-0.220
$B_{s,i}$		0	0.242

membrane module and their impact on the permeate flux and required membrane area. Within this study, the membrane module is discretised into 30 segments. The partial fluxes for a component *i* in a discrete *j* are calculated analogical using Eq. (5) [81].

$$\dot{m}_{j\text{-}1} \cdot w_{i,j\text{-}1} - \dot{m}_j \cdot w_{i,j} = J_{i,j} \cdot A_j \qquad with\, A_{Memb} = \sum A_j \tag{5}$$

The constraints for modelling are the feed concentration and the recovery of the whole membrane module, which determines the outlet concentrations and the feed flux. The partial flux is described using the developed correlation in Section 3.3.2 [Eq. (4)].

3.4 Additional models of unit operations

Besides the three main units responsible for the separation of water and butanol, additional units are necessary for modelling the processes. Those include a flash drum, a decanter for the liquid-liquid phase split between water and butanol, as well as heat exchangers, reboilers and condensers of the column.

Regeneration of the extraction solvent (ionic liquid) is done in a flash drum at a temperature of 80°C and a pressure of 50 mbar. Because of missing property parameters to describe the vapour-liquid equilibrium of this ternary system, the flash is modelled using a split fraction. Water and butanol are evaporated, while $Im_{10,1}$ tcb stays in the liquid phase assuming a negligible vapour pressure of the ionic liquid. To consider a non-ideal separation, a residue fraction of 0.01 g g^{-1} water and butanol in the regenerated ionic liquid are assumed, respectively. The required energy for the evaporation (changing *T* and *p*) is calculated on the basis of heat capacities as well as the heat of evaporation of water and butanol using the correlations given in Aspen Plus® and the correlation for the heat capacity of the ionic liquid (Section 3.2).

In all of the investigated processes, a vapour stream containing water and butanol with azeotropic composition is present. The vapour stream is condensed in a decanter DEC and split into a water-rich and a butanol-rich liquid phase. This separation is fulfilled in a heat exchanger model connected with a decanter model. Because the VLE-HOC parameter set is not able to describe the miscibility gap between water and butanol, the NRTL-LLE parameters from Aspen Plus® are used. All heat exchangers and condenser are modelled with the designated Aspen Plus® models. Reboilers of the columns are implemented in kettle design.

3.5 Cost correlations

The TIC is composed of investments for the flash, distillation and extraction columns (based on [82]); for reboiler, cooler and heater (based on [83]); for membranes and membrane modules (based on [73]); and for decanters (based on [84]). Up-to-date cost indices (Chemical Engineering Plant Cost Indices [85] and Marshall & Swift Cost Indices [86]) are used. Start-up solvent in the integrated extraction-distillation process is considered (based on ionic liquid prices from [87]), additionally. For annual operating costs (TOC), the replacement of the extraction packings, cooling liquid and heating steam mass flows (prices for cooling liquids and heating steam from [34, 88]), replacement of membranes [73, 89] and solvent loss in the extraction (based on ionic liquid prices from [87]) are taken into account. Finally, for the TC, depreciated investment costs over a period of 10 years and annual operating costs are summed up. The cost factors are given in Table 7.

4 Process simulation

The separation task is to deliver ≥3500 kg h^{-1} of butanol with a concentration of >99.8 wt.% assuming a feed concentration of 1 wt.% of butanol in water. This plant capacity correlates to capacities reported by Ni and Sun [28]. For a fair comparison of the three processes, all product streams leaving the process are tempered to the feed entry temperature of 35°C. Each process is designed fixing a set of model parameters that are used as a basis for the subsequent analysis of the influence of different parameters and variables. For each process configuration, the benchmark distillation process (Section 4.1), the integrated extraction-distillation process (Section 4.2) as well as the integrated pervaporation-distillation process (Section 4.3), a base case is simulated fixing a set of process variables. To get a first set of values, a heuristic process design approach was performed.

4.1 Benchmark process

The benchmark process consists of the three units, which are the distillation column C1, the distillation column C2 and the decanter DEC between the columns (see Figure 2). For these units nine design variables are examined: for column C1, feed temperature, feed stage number, bottom-to-feed mass ratio, number of theoretical stages and the

Table 7 Assumptions and cost factors.

Assumptions and cost factors	Value	Unit	Reference	Remarks
Investment costs				
Ionic liquid	30	€ kg^{-1}	[87]	
Membrane modules	200	€ m^{-2}	[73]	
Depreciation period	10	years	[34]	
Heat transfer coefficients	400	W m^{-2} K^{-1}		For cooling
	2000	W m^{-2} K^{-1}		For heating
Tray efficiency	0.7	–		For distillation
HETP	2	m		For extraction
Minimal required temperature difference for heat exchangers	10	K		
Operating costs				
Membrane lifetime	3	years	[73]	
Membrane costs	200	€ m^{-2}	[89]	
Electricity	0.06	€ kW^{-1} h^{-1}	[34]	
Low pressure steam	16	€ ton^{-1}	[34]	T=152°C, p=5 bar
Cooling water	0.05	€ ton^{-1}	[34]	T_{in}=15°C, T_{out}=35°C
Refrigerated water	3.35	€ GJ^{-1}	[88]	T_{in}=5°C, T_{out}=15°C
Low-temperature refrigerant	5.96	€ GJ^{-1}	[88]	T=-20°C

top pressure; for decanter DEC, temperature; and for column C2, bottom-to-feed mass ratio, number of theoretical stages and the top pressure.

The top pressure of both columns is set to ambient pressure so that no additional energy for vacuum or high pressure is necessary. As the product purity of the bottom streams should be high, the number of theoretical stages is set to a value of 20 stages, respectively. To ensure a low butanol loss in the bottom of column C1 and a high butanol amount in the distillate, the feed enters the column above stage 10. Its temperature is increased from 35°C to 50°C before it is fed to the column. In column C2, the feed enters via the first stage as it is a pure stripping column without a reflux stream. With decreasing temperature of the decanter, the butanol weight fraction in the organic stream of the decanter increases as the miscibility gap between the aqueous and the organic phase is widened. However, at the same time, the energy demand for both the condenser to lower the temperature and the feed heat exchanger of column C2 to higher the temperature increase. Owing to these circumstances, a temperature of 60°C was chosen as an initial value. By variation of bottom-to-feed mass ratio in both columns, the mass flow of butanol with a purity of 99.8 wt.% is maximised. All design variables and their obtained values are summarised in Table 8.

With the above-listed base case design parameters, the TIC of €2.2 million and the annual operating cost of €7.8 million are calculated. These result in TC of €0.289 kg^{-1} butanol per year for the separation of butanol from the fermentation broth. The main investment cost drivers (see Figure 6A) are column C1 with 39% as well as the product coolers with 35%. The reason for their large contribution to the investment costs is the large feed stream with low butanol concentrations, which leads to a large column diameter as well as the need for a large heat transfer area for connected heat exchanger units. Table 9 gives an overview about the streams, mass fractions and temperatures within the benchmark process. With a small feed stream in column C2, the investment costs account for a fourth of column C1. Decanter and heater investment costs are 9% and 7% of the TIC, respectively. Seventy per cent of the annual operating costs are generated by column C1 (see Figure 6B). A vast amount of heat steam is necessary to heat and evaporate the feed mass flow of 390,000 kg h^{-1}. Additionally, 17% of the annual operating costs are needed to preheat both column feed streams. The second column C2 and the cooler need 6% each to operate, whereas the costs of the decanter are negligibly low.

Table 8 Base case design variables of the benchmark process.

Design variable	Unit operation	Value	Unit
Feed temperature	C1	50	°C
Feed stage number	C1	10	–
Bottom-to-feed mass ratio	C1	0.99	–
No. of theoretical stages	C1	20	–
Top pressure	C1	1	bar
Temperature	DEC	60	°C
Feed stage number	C2	1	–
Bottom-to-feed mass ratio	C2	0.41	–
No. of theoretical stages	C2	20	–
Top pressure	C2	1	bar

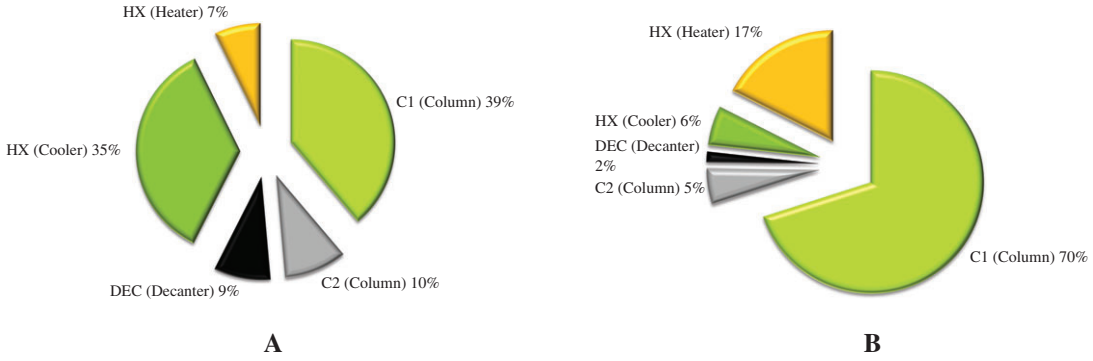

Figure 6 Investment costs (A) and operating costs (B) for the base case design of the benchmark process.
C1 incl. reboiler; C2 incl. reboiler; DEC incl. condenser; HX (Cooler): HX-Water and HX-BuOH; HX (Heater): HX-C1F and HX-C2F.

Table 9 Mass flows, mass fractions and temperatures calculated for the benchmark process.

	Feed	C1-bottom stream	C1-distillate	Aq. phase	Org. phase	C2-distillate
$\dot{m}$ (kg h^{-1})	390,000	386,101	11,380	7481	9534	5635
w_{BuOH} (g g^{-1})	0.010	0.000	0.383	0.061	0.772	0.615
T (°C)	35.0	100.0	96.3	60.0	60.0	94.1

4.2 Integrated extraction-distillation process

Besides the extraction unit EXT of the integrated extraction-distillation process, it is composed of a decanter DEC, a distillation column C2 and flash unit C1. Here, seven design variables are investigated: for extraction column EXT, solvent-to-feed mass ratio, number of theoretical stages and height equivalent to a theoretical plate (HETP) value of the packings; for decanter DEC, temperature; and for distillation column C2, bottom-to-feed mass ratio, number of theoretical stages and the top pressure.

A small solvent-to-feed mass ratio of 0.176 is chosen to decrease the amount of the cost-intensive ionic liquid. To maintain the butanol capacity of ≥3500 kg h^{-1} at the same time, the number of theoretical stages in the extraction column is set to a relatively high value of 10. This column is designed with structured packings assuming an arbitrary HETP value of 2 m. The design variables of decanter and column are not changed compared with the benchmark process. The bottom-to-feed mass ratio of the column is varied to hold the butanol product quality. A summary of all design variables is given in Table 10.

On the basis of these design variables, the TIC sums up to €5.2 million with an annual operating cost of €5.8 million. The TC for the separation of butanol from the fermentation broth amounts to €0.230 kg^{-1} butanol. More than 80% of the investment costs are spent for the first separation step (Figure 7A). Besides the extraction column and required packings, the high costs are caused by the necessary start-up solvent. For the solvent recovery unit, 6% of the TIC are needed. The equipment costs for the further purification of the vapour stream from flash C1 in decanter DEC and column C2 are relatively low compared with the first step and account for 6%. The heat exchanger equipment for preheating the feed of column C2 and cooling of the product streams is negligible because the raffinate stream leaves the extraction column already with 35°C. Only the butanol product stream has to be cooled but the mass flow is low in comparison with the water product stream. Table 11 gives an overview about the streams, mass fractions and temperatures within the extraction-based process.

Table 10 Base case design variables of the integrated extraction-distillation process.

Design variable	Unit operation	Value	Unit
Solvent-to-feed mass ratio	EXT	0.176	–
No. of theoretical stages	EXT	10	–
HETP of the packings	EXT	2	m
Temperature	DEC	60	°C
Feed stage number	C2	1	–
Bottom-to-feed mass ratio	C2	0.498	–
No. of theoretical stages	C2	20	–
Top pressure	C2	1	bar

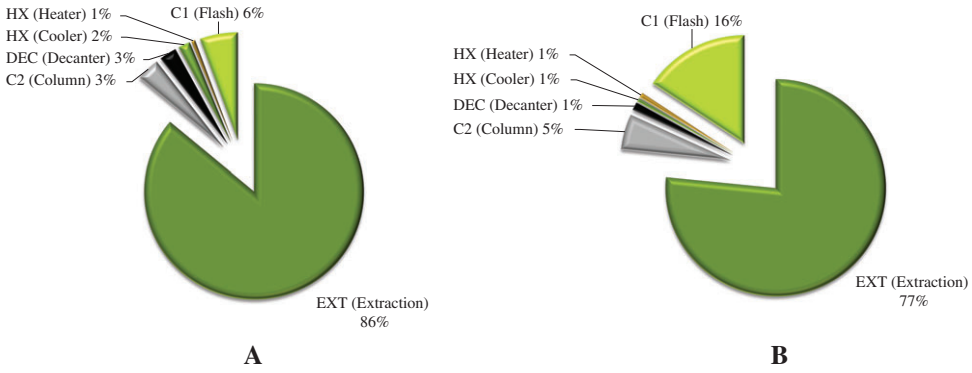

Figure 7 Investment costs (A) and operating costs (B) for the base case design of the integrated extraction-distillation process. C2 incl. reboiler; DEC incl. condenser; HX (Cooler): HX-Flash and HX-BuOH; HX (Heater): HX-C2F.

The main cost driver in the annual operating costs with three-fourths is the extraction column (Figure 7B) due to the solvent loss in the raffinate stream. For the recovery of the solvent present in the extract stream, 16% of the annual operating costs are consumed by the flash column. Only a small part of the costs is allocated to the purification of butanol in the decanter (1%), column C2 (5%), the preheater for column C2 (1%) and finally the product cooler (1%). Concerning the costs for the ionic liquid, it has to be noted that the assumed price is uncertain. The price of €10–30 kg^{-1} reported by Meindersma and de Haan [87] is not necessarily the price that counts for the type of ionic liquid considered in this study. In future studies, the sensitivity of the price for ionic liquid should be investigated.

4.3 Integrated pervaporation-distillation process

The pervaporation-aided process consists of three units – the pervaporation PV, a decanter DEC and the column C. For these units, eight design variables are examined: for pervaporation PV, membrane area (which is determined via a specific recovery), temperature and permeate pressure; for decanter DEC, temperature; and for distillation column C, bottom-to-feed mass ratio, number of theoretical stages and the top pressure.

After the feed mixture has been pumped through the pervaporation membrane module, the concentration of butanol in the retentate is lower than in the feed stream. This decrease in the butanol concentration along the membrane module results in a lowered driving force for permeation of butanol and thus decreases the permeate fluxes and necessitates larger membrane areas. To potentially keep the membrane costs low and simplify the subsequent downstreaming by providing high permeate concentrations of butanol, the butanol recovery for the pervaporation unit was set to a value of 10%. Assuming a recovery rate of >90%, as assumed for the extraction-based process, would result in retentate and permeate concentrations of 0.001 and 0.110 g g^{-1} butanol, respectively, even if the recirculated aqueous stream from the decanter is neglected. For this hypothetical case, the temperature of retentate stream would theoretically fall below 0°C. Also for a recovery rate of 10%, pervaporation leads to a decrease in temperature; therefore, the retentate has to be heated to a temperature of 35°C before it can be recycled back to the fermenter. The pressure on the permeate side of the membrane was defined to 10 mbar, as the highest fluxes are obtained for this permeate pressure. In most pervaporation processes, the permeate pressure is adjusted by the condensation temperature [73]. According to the vapour-liquid equilibrium for binary mixtures of butanol and water, the condensation temperature at 10 mbar is never lower than 5°C. Considering a minimal

Table 11 Mass flows, mass fractions and temperatures calculated for the integrated extraction-distillation.

	Feed	Raffinate	Extract	Aq. phase	Org. phase	C1-distillate	C1-bottom stream	C2-distillate
$\dot{m}$ (kg h^{-1})	390,000	386,175	75,678	3143	7718	6988	68,691	3873
w_{BuOH} (g g^{-1})	0.010	0.000	0.054	0.061	0.772	0.577	0.001	0.548
T (°C)	35.0	35.0	35.0	60.0	60.0	80.0	80.0	92.0

Table 12 Base case design variables of the integrated pervaporation-distillation process.

Design variable	Unit operation	Value	Unit
Butanol recovery	PV	10	%
Feed temperature	PV	35	°C
Permeate pressure	PV	10	mbar
Temperature	DEC	60	°C
Feed stage number	C	1	–
Bottom-to-feed mass ratio	C	0.477	–
No. of theoretical stages	C	20	–
Top pressure	C	1	bar

temperature difference of 10°C between the permeate to be condensed and the refrigerant, it is necessary to use a low temperature refrigerant at -20°C. As the vacuum pump serves solely to remove non-condensable gases from the permeate section, e.g., from leakage streams or fermentation gases such as CO_2 or H_2, which permeate through the membrane, the costs for this pump were neglected. Analogous to the other process configurations investigated, the temperature of the decanter was set to 60°C, the number of stages in the column was set to 20, and the product stream of butanol from the column is provided at a temperature of 35°C. The whole set of design variables is given in Table 12.

On the basis of the specifications given in Table 12, the TIC was calculated to a value of €7.94 million and the total operating costs are €7.51 million year^{-1}. Considering the production capacity of 3500 kg h^{-1} butanol, the annual operating time and the depreciation period, the total investment and operating costs amount to €0.028 kg^{-1} butanol and €0.268 kg^{-1} butanol, respectively. Thus, the total purification cost is €0.296 kg^{-1} butanol. Around 87% of the TIC are attributed to the membrane modules (Figure 8); the required membrane area is calculated to 34,600 m^2. The second largest cost driver in investment costs is the permeate condensator with 6.1% of the TC at a heat exchange area of 1130 m^2. Table 13 gives an overview about the streams, mass fractions and temperatures within the pervaporation-based process. A permeate with a mass fraction of 0.23 g g^{-1} butanol is obtained. The permeate phase splits into an aqueous and organic phase; the aqueous phase mass flow is two times the organic phase mass flow. The aqueous phase, which is fed back to the pervaporation, is circulated within the process, leading to an increased membrane area and higher costs for permeate condensation and permeate heating. Therefore, the membrane costs and the costs for permeate condensation account for a share of 30.7% and 26.2% of the total operating costs. The largest part of the operating costs represents the heater for the retentate stream. Because the large retentate stream of 3,496,492 kg h^{-1} has to be heated up from 32.1°C back to 35°C, the heater consumes 34% of the total operating costs.

5 Conclusion

The production of biobutanol by fermentation processes often suffers from low product titres due to the toxicity of butanol towards the production organisms. Two different process configurations for enabling a continuous separation of butanol from the fermentation were developed and compared with a distillation process for recovery of butanol. On the basis of a fixed set of model parameters, the overall cost for all three processes were determined. For a distillation process employing two columns and a decanter, a purification cost of €0.289 kg^{-1} was estimated for a large-scale production unit. For an integrated extraction-distillation process employing

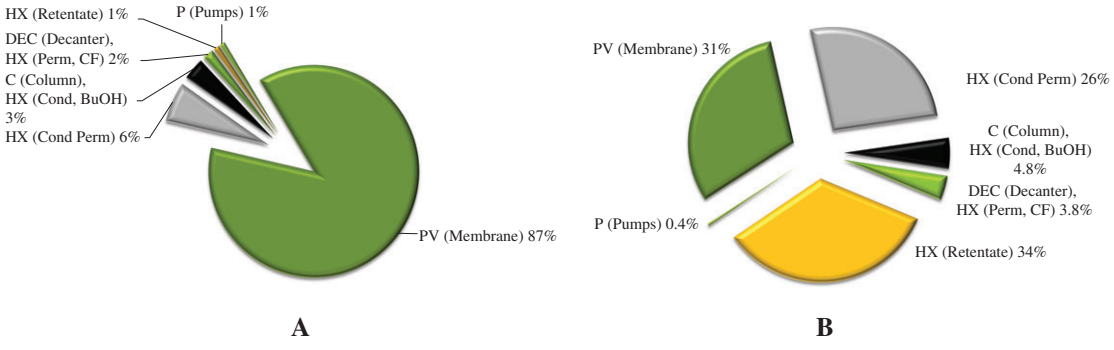

Figure 8 Investment costs (A) and operating costs (B) for the base case design of the integrated pervaporation-distillation process. C incl. reboiler merged with HX-Cond and HX-BuOH; P (Pumps): P-Permeate and P-Feed; DEC merged with HX (Perm) and HX (CF).

Table 13 Mass flows, mass fractions and temperatures calculated for the integrated pervaporation-distillation process.

	Feed	Retentate	Permeate	Aq. phase	Org. phase	C distillate
$\dot{m}$ (kg h^{-1})	3,500,000	3,496,492	19,381	15,872	7348	3841
w_{BuOH} (g g^{-1})	0.010	0.009	0.230	0.061	0.772	0.566
T (°C)	35.0	32.1	5.3	60.0	60.0	93.1

ionic liquids as extraction solvent, a purification cost of €0.230 kg^{-1} was determined. An integrated pervaporation-distillation process allows butanol recovery at the cost of €0.296 kg^{-1} butanol. The downstream costs account for 20% (extraction-distillation), 27% (pervaporation-distillation) and 26% (distillation) of the market price, which was €1.11 kg^{-1} for crude oil-based *n*-butanol in 2012 [90]. To decrease operating costs for all processes, heat integration is necessary.

The costs for extraction- and pervaporation-based purification do not differ significantly from the costs for the distillation process. Thus, they potentially allow a continuous, economical feasible product separation from the fermentation broth, which can increase the fermentation productivity. Furthermore, extraction and pervaporation might benefit from possible changes in the costs for thermal energy. Future research should focus on the sensitivity of the production costs to model parameters and model assumptions. More detailed process analyses are necessary to identify the main cost drivers for the investigated processes. Thus, identification of highly sensitive parameters can contribute to reduced purification costs.

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Appendix

Within this appendix, an overview of the activity models used within the different unit operations (Table A1) as well as the parameter sets for the activity coefficient models are given (Tables A2–A4).

Table A1 Use of NRTL binary interaction parameter sets in the different unit operations.

	Parameter set		
	VLE-HOC	LLE-Aspen	LLE-correlation of Domańska [75]
Distillation columns	×		
Reboiler/condenser	×		
Extraction EXT			×
Flash C1	× (Split fraction)		
Heat exchanger at DEC		×	
Decanter DEC		×	

Table A2 NRTL binary interaction parameters for VLE calculation (VLE-HOC), α=0.3.

Component 1	Component 2	*i*	*j*	a_{ij} (-)	b_{ij} (K)
Water	Butanol	1	2	7.56	-1390.56
		2	1	-1.19	455.48

Table A3 NRTL binary interaction parameters for ternary LLE calculation (LLE-correlation) at 35°C, α=0.2 [75].

Component 1	Component 2	*i*	*j*	a_{ij} (-)
Water	Butanol	1	2	5.22
		2	1	-1.12
Water	$Im_{10.1}$ tcb	1	2	12.32
		2	1	0.06
$Im_{10.1}$ tcb	Butanol	1	2	-1.36
		2	1	0.92

Table A4 NRTL binary interaction parameters for binary LLE calculation (LLE-Aspen), α=0.2.

Component 1	Component 2	*i*	*j*	a_{ij} (-)	b_{ij} (K)	e_{ij} (K)
Water	Butanol	1	2	90.53	-4983.15	-12.06
		2	1	204.23	-9291.70	-30.58

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